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THE FORMATION OF CH^+ IN INTERSTELLAR CLOUDS FROM
MULTIPLY IONIZED CARBON

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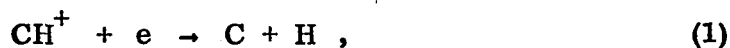
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Abstract

It is suggested that C^{2+} in an ion-molecule reaction with H_2 can initiate molecule production. The production rate by this mechanism may explain the relatively large CH^+ found in diffuse interstellar clouds. The multiply ionized carbon is produced by soft X-ray ionization of C^+ .

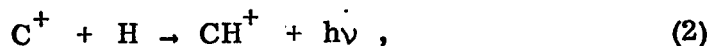
I. Introduction

The observed column densities of CH^+ in diffuse interstellar clouds ($A_V \leq 1-2$ magnitudes) are typically $10^{12} - 10^{13} \text{ cm}^{-2}$ (Adams 1949; Frisch 1972; Hobbs 1973; Cohen 1973; Chaffee 1975). Of several mechanisms suggested for the production of CH^+ , none has provided a satisfactory or consistent explanation of these abundances. Principal among these are grain surface reactions and radiative association. The grain surface reactions (McCrea and McNally 1960; Watson and Salpeter 1972a, b) are estimated to have reaction rates $\sim 10^{-17} - 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ (Watson 1974). These are too slow to explain CH^+ because of the rapid destruction rate for CH^+ by dissociative recombination,



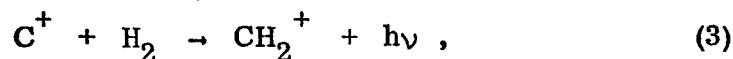
$\beta(\text{CH}^+) \approx 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ (Bardsley and Junker 1973; Krauss and Julienne 1973).

The same objection arises for the radiative association reaction suggested by Bates and Spitzer (1951),

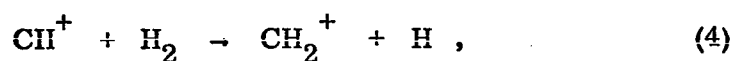


since recent quantum calculations by Abgrall, Giusti-Suzor, and Roueff (1976) yield a reaction rate $k_1 = 1.6 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ at $T \approx 100 \text{ K}$. In view of the abundant evidence for H_2 in interstellar clouds, reactions involving this molecule have also been suggested for initiating the production of other molecules.

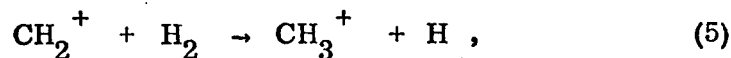
Black and Dalgarno (1973) considered the radiative association of C^+ with H_2 ,



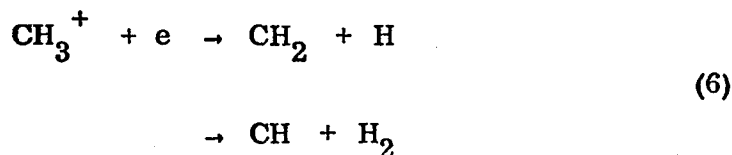
as initiating a sequence of reactions leading to CH and concluded that a reaction rate $k_3 = \text{a few} \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ could explain the CH observations. While the relevant low temperature studies have not been performed, the measurements of Fehsenfeld, Dunkin, and Ferguson (1974) at 90 K suggest a reaction rate $\approx 4 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$. Reaction (3) also leads to CH^+ and its formation has been discussed by Black, Dalgarno, and Oppenheimer (1975). The presence of H_2 , which is necessary for the formation of CH^+ in their scheme, also destroys CH^+ (Black and Dalgarno 1973; Watson 1974),



at a typical ion-molecule reaction rate $k_4 = 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. Reaction (4) is followed by either dissociative recombination, $CH_2^+ + e \rightarrow CH + H$ (reaction rate $\beta(CH_2^+) = 10^{-7} \text{ cm}^3 \text{ s}^{-1}$), the ion-molecule reaction



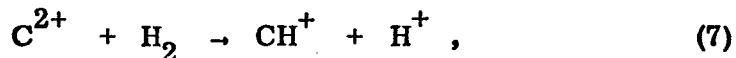
$k_5 = 7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, or photodissociation, $CH_2^+ + h\nu \rightarrow CH^+ + H$. The CH_3^+ is destroyed primarily by dissociative recombination,



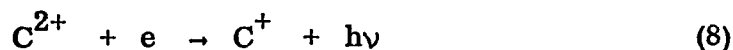
with a total reaction rate $\beta(\text{CH}_3^+) = 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ (the branching ratios for this reaction are not known). Black et al. (1975) have suggested that the difficulty presented by reaction (4) can be avoided if some of the following conditions hold: the photodissociation rates for CH_2^+ and CH_3^+ are large; in reaction (6) the branching ratio favors formation of CH_2 ; and that photoionization dominate photodissociation of CH_2 . Their scheme amounts to recycling the CH^+ efficiently, avoiding the formation of CH which can be photodissociated thus ending the cycle. Some CH does return to the cycle, however, since it is photoionized to CH^+ at a rate about twice that of photodissociation. Blint, Marshall, and Watson (1976) calculate photodissociation rates for CH_3^+ and find them to be unimportant compared to dissociative recombination. Despite these attempts to minimize the effects of reaction (4) (and further tests of the other assumptions are certainly necessary), the production scheme of Black et al. (1975) requires postulating a large reaction rate $\approx 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ for reaction (3). A number of other suggestions for producing CH^+ will not be discussed here but are criticized in a recent review by Dalgarno and Black (1976), and have been reevaluated by Barsuhn and Walmsley (1976).

II. C^{2+} Reactions

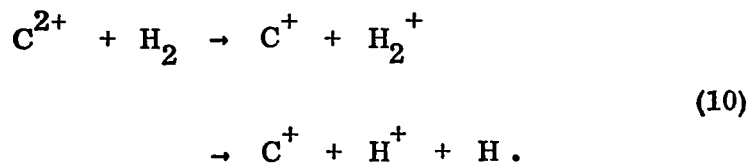
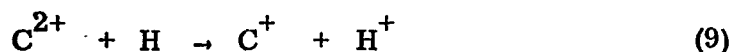
We suggest that another channel may exist for initiating molecule production beginning with doubly ionized carbon undergoing an exothermic ion-molecule reaction with H_2 ,



where we use the notation $\text{C}^{2+} \equiv \text{CIII}$, etc. The production of C^{2+} from X-ray ionization of C^+ will be discussed later. No measurements or calculations exist for reaction (7), however, its importance for molecule production depends on its reaction rate compared to radiative recombination,



and charge exchange reactions with hydrogen,

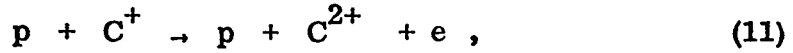


Charge transfer reactions in multiply charged ion-atom collisions have previously been discussed in the context of determining the physical conditions in interstellar clouds from column density measurements of multiply ionized atoms (Weisheit 1973; Steigman, Kozlovsky, and Rees 1974). Steigman (1975) has discussed charge transfer reactions of the type, $\text{A}^{2+} + \text{H} \rightarrow \text{A}^+ + \text{H} + \Delta E$ and $\text{A}^{3+} + \text{H} \rightarrow \text{A}^{2+} + \text{H}^+ + \Delta E$, and concludes that most, if not all, of these reactions will be rapid ($k \approx 10^{-14} - 10^{-9} \text{ cm}^3 \text{ s}^{-1}$), if the curve crossing distance $R_c \leq 12\text{\AA}$, a condition satisfied for C^{2+} and C^{3+} . Blint, Watson, and Christenson (1976) have calculated a reaction

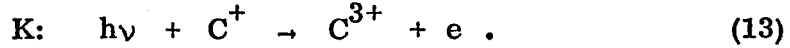
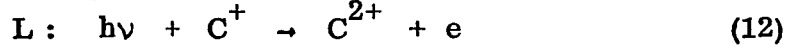
rate $\sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for $10^3 \leq T \leq 2 \times 10^4 \text{ K}$ for the charge exchange $\text{C}^{3+} + \text{H}$. The charge-exchange cross-sections for $\text{C}^{2+} + \text{H}$ are apparently negligibly small (McCarroll 1975). Experimental data for these reactions is lacking, but information for reactions of the type (7), (9), and (10) does exist. Spears et al. (1972) have studied partial charge transfer reactions at room temperature for Mg^{2+} and Ca^{2+} with xenon and a variety of molecular targets. For xenon, the only atomic target, they find a reaction rate $5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$; considerably less than the Langevin rate, $2.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. In contrast, for most of the molecular targets, they find large coefficients $\approx 5.6 \times 10^{-10} - 1.8 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (of the order of the Langevin rate); for the one case with a large $R_c \approx 12\text{\AA}$, a smaller rate, $1.6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ was found. In the case of Mg^{2+} with NO_2 , a fast binary reaction was measured, $\sim 1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, and both partial charge transfer and exothermic reactions (e.g. $\text{Mg}^{2+} + \text{NO}_2 \rightarrow \text{NO}^+ + \text{MgO}^+$) were present although the branching could not be ascertained; a similar situation probably exists for Ca^{2+} .

The relative efficiency with which C^{2+} initiates molecule production is, $\eta = \frac{1}{2} f k_6 / (\alpha(\text{C}^{2+}) x(e) + \frac{1}{2} f(k_6 + k_9) + (1-f) k_8)$, where $f = 2n(\text{H}_2)/n$, $n = n(\text{H}) + 2n(\text{H}_2)$, and $\alpha(\text{C}^{2+}) = 7 \times 10^{-10} \text{ T}^{-0.7} \text{ cm}^3 \text{ s}^{-1}$. Typically, the fractional abundance of electrons in interstellar clouds, $x(e) \approx 10^{-4}$ and radiative recombination can be neglected if charge-exchange rates are $\geq 10^{-15} \text{ cm}^3 \text{ s}^{-1}$. If, as has been suggested, $k_9 \ll (k_7 + k_{10})$ then for some small value of $f \approx k_9/(k_7 + k_{10})$, $\eta = k_7/(k_7 + k_{10})$ which we take ≈ 1 . In other words, each C^{2+} which is created leads to CH^+ in regions with some small fractional abundance of H_2 .

Multiply ionized carbon can be produced in interstellar clouds from direct cosmic ray ionization,



and L and K shell photoionization by soft X-rays,



The K-shell photoionization is generally followed by an Auger transition and it is assumed in (13) always to result in the formation of C^{3+} . In interstellar clouds C^{3+} is rapidly returned to C^{2+} by either radiative recombination, or charge exchange reactions with hydrogen (rate $\sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, Blint et al. 1976). The effective formation rate of C^{2+} is given approximately by the ionization rate of C^+ , $\zeta^T(C^+) = \zeta^P(C^+) + \zeta^{XR}(C^+)$, where $\zeta^{XR}(C^+) = \zeta^K(C^+) + \zeta^L(C^+)$. This result will not be altered appreciably if C^{3+} undergoes a reaction similar to (7), since we assume that most of the ionized C^+ enters the molecular cycle ($\eta \approx 1$). The cosmic ray ionization rate for C^+ $\zeta^P(C^+) = 1.3 \zeta^P(H)$, where $\zeta^P(H) \sim 10^{-17} - 10^{-16} \text{ s}^{-1}$ is the primary cosmic ray ionization rate on hydrogen. The ionization rate by X-rays is a function of the L and K shell cross-sections, $\sigma(E)$, the soft X-ray flux, $\phi(E)$, the attenuation of these X-rays by He, H, and H_2 in the cloud, and the energy E (here expressed in keV). It appears from the available information that K-shell ionization dominates photoionization in diffuse clouds, since these photons with $E > 0.28 \text{ keV}$ have an attenuation length $N_1(E) \gtrsim 5 \times 10^{20} \text{ cm}^{-2}$. At decreasing energies the attenuation length becomes very small because the relevant photoionization cross-sections of H, H_2 , and He vary roughly as E^{-3} (at $E = 0.15 \text{ keV}$, $N_1 \approx 6 \times 10^{19} \text{ cm}^{-2}$). For the L-shell ionization we use the fit suggested by Henry (1970), since the

similar fit to $\sigma(\text{Cl})$ agrees well with the measurements by Denne (1970). For the K-shell we find that $\sigma^{\text{K}}(\text{C}^+) = \sigma_{\text{th}}(E/E_{\text{K}})^{-2.3}$ near threshold ($E_{\text{K}} \leq E \leq 2 E_{\text{K}}$) fits the calculations of McGuire (1968) as well as the few measurements presently available (Denne 1970; Bearden 1966).

Silk (1973) has reviewed the recent observations of the diffuse soft X-ray flux down to 0.1 keV. Below 1 keV, the data can be roughly fit in a number of energy bands. (Silk 1973; Glassgold and Langer 1973). Extrapolating from above 1 keV, $\phi(E) = 12.4 E^{-1.7}$ for $E > 0.23$ keV.; $\phi(E) = 1.11 E^{-3.33}$ for $0.23 \geq E \geq 0.15$ keV.; and $\phi(E) = 2.8 \times 10^{-4} E^{-7.7}$ for $0.15 \geq E \geq 0.1$ keV, where $\phi(E)$ is in photons/(cm² s ster keV). At best these fits represent some rough average to the data which otherwise varies considerably with position in the sky, energy band surveyed, and experiment. For example, $\phi(0.23) \doteq 150$, while reliable measurements of the flux in the range 0.21-0.28 keV vary from ~ 100 -500 photons (cm² s ster keV)⁻¹. Similarly, sky maps of the galaxy at 0.8 keV show many regions of enhanced flux (~ 2 -3) above the extrapolated fit. In particular surveys at $E \geq 0.3$ keV would be important for the problem discussed here, since ionization at the K-edge dominates photoionization of C^+ throughout all but the outermost regions of diffuse clouds. The previously defined fits to $\phi(E)$ and $\sigma(E)$ give the following photoionization rates: $\zeta^{\text{K}}(\text{C}^+) \approx 10^{-15} \text{ s}^{-1}$; $\zeta^{\text{L}}(\text{C}^+) \approx 2 \times 10^{-16} \text{ s}^{-1}$ for $E > 0.15$ keV; and $\zeta^{\text{L}}(\text{C}^+) \approx 2 \times 10^{-14} \text{ s}^{-1}$ for $E > 0.1$ keV. While the ionization rate increases with decreasing energy, these photons are sharply attenuated; photons with $E > E_{\text{K}}$ can, however, readily penetrate diffuse clouds. In this initial discussion of the role of C^{2+} in molecule production, the details of the radiative transfer of the photon field will be ignored, and we will only consider the photoionization rate due to photons with $E > E_{\text{K}}$. In this case $\zeta^{\text{T}}(\text{C}^+) \approx 10^{-15} \text{ s}^{-1}$, but it

should be noted for later discussion that this rate could be a factor of 4-5 larger in some regions due to the diffuse background and even larger in the presence of discrete sources.

III. CH^+ Abundance

In diffuse clouds where most of the carbon is ionized the fractional abundance of CH^+ , $x(\text{CH}^+) = n(\text{CH}^+)/n$, can be put in the following form:

$$x(\text{CH}^+) = \frac{[(1-f) k_2 + \frac{1}{2} f k_3 \theta + \zeta^T(\text{C}^+)/n] x(\text{C}^+)}{\beta(\text{CH}^+) x(e) + \frac{1}{2} f k_4 \epsilon + g_d(\text{CH}^+)} \quad (14)$$

where $g = G/n$, $G(X)$ is the photodestruction rate for species X , and d and i refer to dissociation and ionization respectively. The terms ϵ and θ are essentially recycling factors for the efficiency with which CH^+ destroyed by H_2 , reaction (4), returns to CH^+ (the limits on these terms are, $1 \geq \epsilon$, $\theta \geq 0$). For illustrative purposes reactions of C^+ with CH and CH_2 will be neglected (valid for $n \leq 10^3 \text{ cm}^{-3}$). If $z = \beta(\text{CH}_2^+) x(e) + \frac{1}{2} f k_5 \gg g_d(\text{CH}_2^+)$ then the following approximate forms hold: $\epsilon \approx g_d(\text{CH})/g(\text{CH})$ and $\theta \approx g_i(\text{CH})/g(\text{CH})$, which are about 1/3 and 2/3, respectively, for the standard interstellar radiation field (Habing 1968). If photodissociation of CH_2^+ is an important destruction mechanism (Black et al. 1975), then at sufficiently low densities such that $\beta(\text{CH}_2^+) x(e) + \frac{1}{2} f k_5 \ll g_d(\text{CH}_2^+)$, $\theta \approx 1$ and $\epsilon \approx z/(z + g_d(\text{CH}_2^+)) g_d(\text{CH})/g(\text{CH})$. This second case recycles CH^+ efficiently in regions where it is rapidly destroyed by H_2 .

From equation (14) it can be seen under what conditions C^{2+} reactions can dominate production of CH^+ . In regions where $f > f_c$, a critical value such that $\eta \approx 1$ ($10^{-3} < f_c < 10^{-1}$) reaction (7) will be more important than radiative association reaction (1) if $y_1 = (1-f) k_2 / (\zeta^T(C^+)/n) < 1$; in appropriate units $y_1 \approx 1.6 \times 10^{-2} n / \zeta_{-15}^T(C^+)$, so that $y_1 < 1$ for $n < 100-500 \text{ cm}^{-3}$ for $\zeta^T(C^+)/10^{15} \approx 1-5$. The comparison with the radiative association reaction (3) gives, in appropriate units, $y_2 \approx 3 \times 10^{-3} f_{-1} n (k_3/10^{16}) / \zeta_{-15}^T(C^+)$. For small f , where CH^+ is probably found, C^{2+} production dominates for $n \sim 100-500 \text{ cm}^{-3}$ if $(k_3/10^{16}) \approx 3$, the value suggested to explain CH in diffuse clouds). These results will vary with k_3 , so that the C^{2+} reaction is less important for CH^+ production if $k_4 = 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, the value suggested by Black et al. (1975) as necessary to explain CH^+ measurements. It will be more important if the experimentally estimated rate at 90 K, $k_3 = 4 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$, is more typical of its value (Fehsenfeld et al. 1974). It seems likely that the mechanism we propose here to produce CH^+ is important over some range of densities and f appropriate to diffuse interstellar clouds. In the remainder of this discussion we will explore only the contribution of reaction (3) to CH^+ , which, in appropriate units, is given by,

$$x(CH^+) = 10^{-8} \frac{\zeta_{-15}^T(C^+)/n \cdot x_{-4}(C^+)}{\beta_{-7}(CH^+) x_{-4}(e) + 5f_{-1} \epsilon} \quad (15)$$

In low density regions with small values of $f \leq 0.1$, if $g_d(CH_2^+) \gg z$, then $\epsilon < 0.1$ and $x(CH^+) \approx 10^{-8} \zeta_{-15}^T(C^+) / (\beta_{-7}(CH^+) n)$, since $x(e) \approx x(C^+)$. From this expression it is obvious that values of $x(CH^+) \approx 10^{-9} - 5 \times 10^{-9}$ can be achieved at low densities, $n \approx 10$, and ionization rate $\zeta^T(C^+) \sim (1-5) \times 10^{-15} \text{ s}^{-1}$.

While these fractional abundances are not inconsistent with the measurements of Cohen (1973), Hobbs (1973), and Chaffee (1975), the interpretation of these results is complicated by the fact that they measure column densities and equation (15) gives only the local density. In the direction of many of the stars where CH^+ is observed, substantial column densities of H_2 ($F = 2N(\text{H}_2)/N > 0.1$) have also been found (Spitzer et al. 1973). These clouds probably consist of an inner core with large f (small $x(\text{CH}^+)$) and an outer part with small f (large $x(\text{CH}^+)$). Two component models for diffuse clouds are supported by observation; Morton (1975), for example, in a detailed study of ζ Oph, found some HI and all CH^+ to be in a cloud component with a heliocentric velocity -12.6 km s^{-1} , while some HI, all H_2 , and most CH was in a component at -14.4 km s^{-1} . Thus, in the outer parts of diffuse clouds, larger local abundances $x(\text{CH}^+) \approx 10^{-8}$ might be required to explain the column density measurements of CH^+ . Whether the C^{2+} mechanism for producing CH^+ described here can adequately explain $N(\text{CH}^+)$ in diffuse clouds will depend on details of the cloud profile, n , $\phi(E)$ at $E \approx 0.3 \text{ keV}$, and possibly the contribution of the softer X-rays at $E \sim 0.1-0.15 \text{ keV}$. We expect to report on detailed cloud models of $N(\text{CH}^+)$ in a future publication. Observations of some anomalously large $N(\text{CH}^+)/N \sim \text{a few} \times 10^{-8}$ in 20 and 23 Tau may result from a locally enhanced soft X-ray flux. It should be emphasized again that more and better observations of the soft X-ray flux towards stars containing CH^+ would be most useful in establishing the applicability of the model discussed here.

There are no direct observations of C^{2+} in diffuse clouds containing CH^+ , which is unfortunate, since $\zeta^T(\text{C}^+)/n \sim k_7 x(\text{C}^{2+})f^{-1}/x(\text{C}^+)$. However, the observed upper bounds on $N(\text{C}^{3+})$ place limits on $\zeta^k(\text{C}^+)/n$. From the balance equations $\zeta^K(\text{C}^+)/n \approx N(\text{C}^{3+})/N(\text{C}^+) k_{ce}$, where k_{ce} is the charge exchange reaction

rate for C^{3+} with hydrogen. If $k_{ce} \approx 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (as may be indicated by the calculations of Blint et al. 1976), then Morton's (1975) data for ζ Oph yields $\zeta^K(C^+)/n \leq 8 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, which is not inconsistent with the model presented here (a value $\sim 10^{-15}$ would explain the ζ Oph observations).

IV. CH Abundance

Reaction (7) also contributes to the production of CH in diffuse clouds. If f is large enough that $\frac{1}{2}fk_4 \epsilon \gg \beta(CH^+)x(e)$, then the CH^+ abundance will decrease, being rapidly channeled to CH, and the CH abundance will increase. In regions with large enough f values the CH abundance is,

$$x(CH) \approx \frac{[(1-f)k_2 + \frac{1}{2}fk_3 + \zeta^T(C^+)/n]x(C^+)}{g_d(CH) + k_{17}x(C^+)} \quad (16)$$

where $k_{17} = 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ is the reaction rate for destruction by $C^+ + CH \rightarrow C_2^+ + H$. The charge exchange reaction, $C^+ + CH \rightarrow CH^+ + C$, can be neglected because CH^+ is rapidly returned to CH. The destruction rate may be smaller than k_{17} because the C_2^+ leads to $C_2H_2^+$ which may dissociatively recombine to 2CH (Barsuhn and Walmsley 1976). This recombination could enhance CH at high densities where C^+ dominates destruction; unfortunately, its branching ratio is not known (the other channel is $C_2H + H$).

For $n \leq 10^3 \text{ cm}^{-3}$, the contribution to CH from C^{2+} alone yields, $x(CH) \approx (\zeta^T(C^+)/G_d(CH))x(C^+) = 10^{-9} \zeta_{-15}^T(C^+) \exp(-\tau_{XR} + \tau_d(CH))$, where $G_d(CH) = 10^{-10} \text{ s}^{-1}$ at the outside of a cloud for the Habing (1968) radiation field. To explain the observed values $x(CH) \approx 2 \times 10^{-8}$ (Cohen 1973; Chaffee 1975) in diffuse

clouds, $\zeta^T(C^+)$ would have to be about 10^{-13} s^{-1} . The attenuation of the 0.3 keV X-rays ($\tau_{XR} \approx N/5 \times 10^{20} \text{ cm}^{-2}$) is only partially offset by the attenuation of the ultraviolet photons which dissociate CH ($\tau_d(CH) \approx N/1.3 \times 10^{21} \text{ cm}^{-2}$). Again while these large values of $\zeta^T(C^+)$ are not suggested by the observed diffuse X-ray flux, they are not inconsistent with the upper limits set by $N(C^{3+})$. Throughout we have used the Habing (1968) radiation field, though values somewhat larger than this ($\sim 2-8$) are suggested by the work of Jura (1974). While this increase does not substantially affect the results for CH^+ , it does place more stringent conditions on the value of $\zeta^T(C^+)$ if CH is to be explained. Equation (16) suggests that radiative association can explain the observed $N(CH)$ if $k_3 \approx \text{a few} \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$, $f \gtrsim \frac{1}{2}$, and $n \approx 10^2 \text{ cm}^{-3}$ when the Habing radiation field is used; the same requirements have already been noted by Black and Dalgarno (1973) ^{Dalgarno and Black,} (1976) and Barsuhn and Walmsley (1976).

In conclusion, we have suggested a new mechanism for molecule production which could be important for the production of CH^+ in diffuse interstellar clouds. Conceivably this C^{2+} ion-molecule reaction and the $C^+ + H_2$ radiative association reaction could explain both the CH^+ and CH observed. Further studies of reaction (7) and the soft X-ray flux are necessary to understand the importance of C^{2+} .

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